

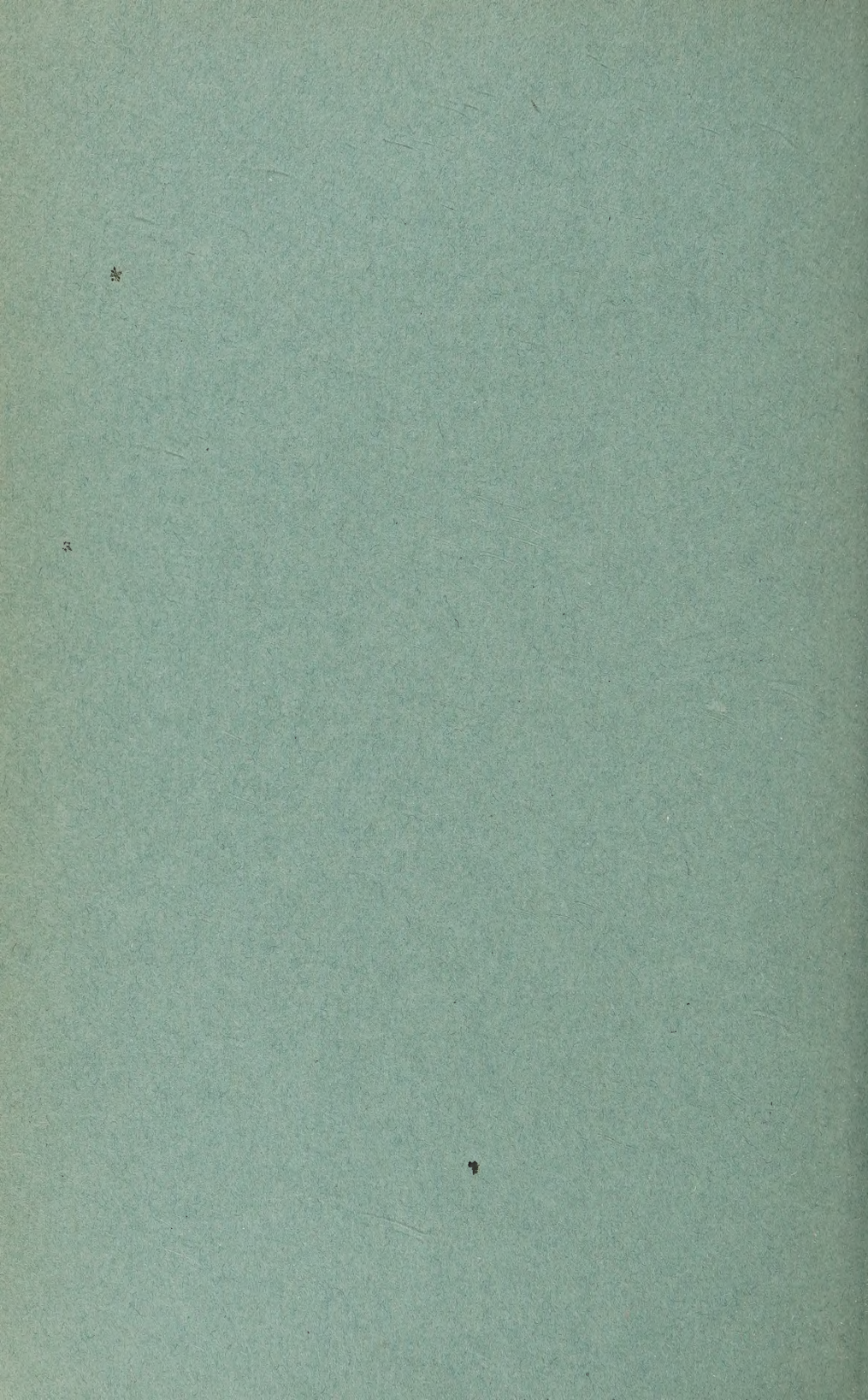
A STUDY
OF THE
QUANTITATIVE DETERMINATION
OF
ANTIMONY

By
LEWIS ADDISON YOUTZ, PH. M.

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF
PURE SCIENCE OF COLUMBIA UNIVERSITY

NEW YORK CITY
1902

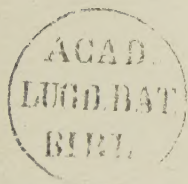


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INTRODUCTION.

THE work of this thesis was undertaken for the purpose of studying, first, the volatility of the chlorides of antimony and of tin in an hydrochloric acid solution, with a view toward their separation after the manner of the separation of arsenic from other metals in the well-known Fischer's distillation method; and second, some of the volumetric methods heretofore used for the estimation of antimony, to test carefully their limits of accuracy, and to determine which method seemed best adapted for ordinary use.

In connection with this latter work there came up naturally the question as to the completeness of the oxidation of antimony by nitric acid, and by potassium chlorate, and of its reduction by the various agents usually employed in its reduction.

Incidentally the discovery of a constant unaccountable discrepancy of about 1 per cent., when sodium thiosulphate solution was standardized against metallic antimony, or against copper, iodine, and potassium bichromate led to a question as to the correctness of the atomic weight of antimony as usually taken.

L. A. Y.

QUANTITATIVE CHEMICAL LABORATORY,
HAVEMEYER HALL, COLUMBIA UNIVERSITY,
May 1, 1902.

ACKNOWLEDGMENT.

THIS work was undertaken at the suggestion of Professor Edmund H. Miller, and carried out under his direction.

I take this opportunity of expressing my deep appreciation of his ready counsel and valuable assistance throughout the work, for whatever merit it may possess is due to his kindly interest and careful supervision.

L. A. Y.

QUANTITATIVE CHEMICAL LABORATORY,
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A STUDY OF THE QUANTITATIVE DETERMINATION OF ANTIMONY.

PART I.

VOLATILITY OF ANTIMONY CHLORIDES AND TIN CHLORIDES IN CONCENTRATED HYDROCHLORIC ACID.

HISTORICAL.

THE volatility of these chlorides with hydrochloric acid, chlorine, or some substance which would form a chloride with them, as mercuric chloride, has been observed from an early date. In the case of antimony trichloride the method was first used to make it pure (Basilius Valentinus-Glauber, 1648). Stannic chloride was first prepared by the distillation of tin in the presence of mercuric chloride in 1611.

This property of the volatility of the chlorides seems not to have suggested a means of separating the metals, however, until more recently, at least no record has been made until in 1825 H. Rose¹ found it possible to distil antimonious chloride from sulphides of antimony by hydrochloric acid. Wöhler² separated arsenic, antimony and tin, as chlorides, from other metals as iron, lead, etc., by leading chlorine over their sulphides contained in a heated tube.

Schneider³ was able to distill arsenious chloride, contained as an impurity in organic compounds, by the use of concentrated hydrochloric acid. He states that the arsenious chloride begins to go over at 100° C. This separation was extended by Fischer⁴ to the separation of arsenic from metals, and perfected so as to be a complete separation in 1881. Classen⁵ separated antimony from copper by heating with ammonium chloride. In 1894 Jannash⁶ reported the separation of arsenic, antimony, and tin from other metals by

¹ Pogg. Ann., 3, 441, 1825.

² Ann., 73, 374, 1850.

³ Wein. Acad. Ber., VI., 409 (1851).

⁴ Ber., 13, 1881.

⁵ Zeit. f. Anal. Chem., 18, 388 (1879).

⁶ Ber., 3, 1894.

hydrochloric acid gas stream in a porcelain boat. He gives no figures as to the completeness of the separation. In 1895¹ Andrews, in the analysis of alloys of lead, arsenic, antimony, and tin, found complete separation of arsenic, antimony, and tin in a dry hydrochloric acid stream only when the gas had been led through concentrated nitric acid. Moyer² found the separation of antimony from lead, and copper complete, when the hydrochloric acid gas was lead over their oxides in a tube heated to a temperature of about 200° C. In the same year Kelly and Smith³ reported that antimony, and stannic tin were completely volatilized when a hydrochloric acid gas stream was lead over their sulphides at a somewhat raised temperature. Stannous sulphide however was not volatilized except in small part.

TESTING THE VOLATILITY OF ANTIMONY AND TIN CHLORIDES.

In all these cases, however, except those of Schneider and Fischer, the conditions of volatilization were different from those contemplated in this research. In those mentioned the volatilization takes place at or near the volatilizing point (boiling point) of the dry chloride of either arsenic, antimony or tin, the latter in the stannic condition. The respective boiling points of these have been given as 134° C. for arsenious chloride, 223° C. for antimonious chloride, and 114° C. for stannic chloride. These temperatures for the chlorides of antimony and tin were verified as approximately correct many times in the course of this research.

The volatilizing temperature of the chlorides in a water solution of hydrochloric acid is not always that of the dry chloride salt. In the case of tin the temperature at which the stannic chloride goes over in the aqueous hydrochloric acid solution is approximately that of the boiling point of dry stannic chloride, *i. e.*, 114° C., as shown by the results given below. Antimonious chloride, however, goes over at a temperature much below that of 223° C. In fact it began going over where the boiling point of aqueous hydrochloric acid becomes constant, *i. e.*, at about 108° C. The arsenious chloride goes over at even a lower temperature than this, as it begins to go

¹J. Am. Chem. Soc., 17, 869-873 (1895).

²J. Am. Chem. Soc., 1896.

³J. Am. Chem. Soc., 1896.

over as soon as the acid gas begins to leave the solution rapidly at about 75°C. to 80°C. for concentrated acid, or even below this temperature. There seems to be a misconception here on the part of some chemists regarding the volatilizing point of arsenious chloride in aqueous hydrochloric acid. In a recent edition (1901) of Prescott and Johnson's *Qualitative Analysis* the temperature of the volatilization of the arsenic in the usual Fischer's distillation is given at 132°C. , and Janasch¹ gives the temperature as 134°C. This latter is the boiling point of dry arsenious chloride. However it is impossible to get so high a temperature as 134°C. for aqueous hydrochloric acid at the ordinary atmospheric pressure. It boils, beginning at about 35°C. the temperature rising gradually till at about 107°C. – 108°C. the temperature for New York City remains constant, and the per cent. of acid here remains constant at about 20 per cent. acid until the whole solution is evaporated. This is in accord with the well-known fact that water containing hydrochloric acid, hydrobromic acid, or iodic acid cannot be completely freed from the acids by boiling, as after a time as the boiling proceeds, the relative amounts of acid and water remains constant for each acid. It was found that the addition of ferrous sulphate in such quantities as is customary in Fischer's distillation method for arsenic has but little effect on the boiling point of the solution, raising it only 3 or 4 degrees and of course not affecting the temperature of the vapor. Remsen² gives the temperature at which the arsenic begins to go over as 100°C. Schneider,³ who first suggested this method of distillation, also gives the temperature as 100°C.

EXPERIMENTAL.

In order to test the method of distillation of antimony and tin chlorides, a certain amount of the chloride was measured into a side-necked distilling flask fitted with a condenser, and a two-hole stopper with two thermometers, one thermometer reaching into the boiling solution to record the temperature of the liquid, and the other reaching to the level of the exit tube to measure the temperature of the vapor. The solution of the chlorides, to which was added from 50 c.c. to 150 c.c. of concentrated hydrochloric acid, was distilled in

¹ *Gewichts Analyse* (1897), p. 176.

² *Inorganic Chemistry*, p. 317, 1898.

³ *Wein. Acad. Ber.*, VI., 409, 1851.

fractions, each fraction distilling over being collected in a vessel containing water and tested for antimony or tin by sulphuretted hydrogen gas. 25 c.c. or 50 c.c. of a standard approximately tenth normal solution of either antimony or tin (calculated to the metal) were taken for each experiment. In the case of stannous chloride however the temperature only of the vapor was recorded and a much larger quantity of the salt was taken for each distillation. The results for the four salts, *i. e.*, stannous chloride, stannic chloride, antimonious chloride, and antimonie chloride are tabulated below.

Experiment 1.—Stannous Chloride.

100 c.c. of *n*/10 stannous chloride (pure Kahlbaum's) were taken, 150 c.c. of concentrated hydrochloric acid added, also a large portion of zinc chloride, and the distillation proceeded with. The temperature of the vapor rose gradually to 107°–108° and no tin was found in the distillate. The distillation was continued till the vapor showed a temperature of 150° C., when only a nearly dry salt remained in the flask. This distillate showed some tin, though only a very small fraction of the amount taken. The tin distilled was in the stannic condition.

Experiment 2.—Stannous Chloride.

In this experiment several grams of metallic tin were placed in a flask with about the same amount of strong hydrochloric acid as in the previous experiment, this allowed to act for some time, then zinc chloride added and the distillation carried out as in experiment 1. Little more than traces of tin distilled over and these only when the vapor temperature rose to 110°–115°. The tin in the distillate was in the stannic condition.

Experiment 3.—Stannic Chloride.

25 c.c. of *n*/10 stannous chloride solution was first treated with potassium chlorate and large excess of hydrochloric acid, then zinc chloride was added and more hydrochloric acid. The results of the distillation were as follows :

Fraction.	B. P. Liquid.	Vapor Temp.	Tin Found by H ₂ S in the Distillate.
1	110°–111°	107°–107.5°	Nothing.
2	112–114	107–108	“
3	114–117	108	“

From this point a stream of hydrochloric acid gas was run through the boiling solution.

Fraction.	B. P. Liquid.	Vapor Temp.	Tin Found by H_2S in the Distillate.
4	117°-125°	108°	Nothing.
5	125-185	111	Heavy precipitate of SnS_2 .
6	185-220	110-108°	" " " "

More hydrochloric acid (concentrated) was added and the distillation continued with a stream of hydrochloric acid gas.

Fraction.	B. P. Liquid.	Vapor Temp.	Tin Found by H_2S in the Distillate.
7	120°-162°	108°	Considerable SnS_2 .
8	162-185	109	" "
9	185-195	105-108°	" "

The residue in the flask was here treated, after dilution with water, with hydrogen sulphide. Not over half of the stannic chloride had been distilled over, and what went over was mostly in the fifth and sixth fractions.

Experiment 4.—Stannic Chloride.

This was tried to determine the effect of sulphuric acid. Stannous chloride (25 c.c. $n/10$ solution), was oxidized by aqua regia, a large excess of concentrated hydrochloric acid added, then 25 c.c. of strong sulphuric acid. No stannic chloride distilled over after repeated distillations. Temperature as high as 220° C. Stannic sulphate remained as a non-volatile product.

Experiment 5.—Antimony in Antimonious Condition.

25 cc. of the antimonious chloride ($n/10$) solution were taken and oxidized by nitric acid and excess of hydrochloric acid.

Fraction.	B. P. Liquid.	Temp. Vapor.	Antimony Found by H_2S in Distillate.
1	111°-112°	105°-106°	Nothing.
2	112-119	106-107	"
3	119-125	107	"
4	125-130	107	"
5	130-145	107	"
6	145-185	107-108	Trace.

Experiment 6.—Antimony in Antimonic Condition.

The same amount of antimony solution as in experiment 5, oxidized by aqua regia, and excess of hydrochloric acid, then large amounts of zinc chloride added to raise the boiling point.

Fraction.	B. P. Liquid.	Temp. Vapor.	Antimony Found by H_2S in Distillate.
1	106°	100°	Nothing.
2	106°-110°	100°-106°	"
3	110-117	106-106.5	"
4	117-145	106.5-107	"
5	145-185	107-108	Trace.
6	185-275	108-115.5	Just enough to see the ppt.

Experiment 7.—Antimony in Antimonie Condition.

To the residue of experiment 6, more hydrochloric acid was added and then the distillation carried on with a stream of hydrochloric acid gas.

Fraction.	B. P. Liquid.	Temp. Vapor.	Antimony in Distillate.
1	120°-145°	107°	Nothing.
2	145-185	108	Trace.
3	185	112	"

Experiment 8.—Antimony in Antimonie Condition.

10 grams of antimonious chloride (the dry salt) were taken, several grams of potassium chlorate and a large excess of hydrochloric acid were added and distilled.

Fraction.	B. P. Liquid.	Temp. Vapor.	Antimony in Distillate.
1	112°	107°	Trace.
2	113	108	"
3	113	108	Nothing.

Experiment 9.—Antimony in Antimonie Condition.

Zinc chloride and more concentrated hydrochloric acid added to the residue of experiment 8, and the distillation repeated.

Fraction.	B. P. Liquid.	Temp. Vapor.	Sb in Distillate.
1	108°-110°	107.5°	Trace.
2	110-111	108	Nothing.
3	111-120	108	"
4	120-130	108-109	Trace.
5	130-155	109-111	Slight ppt.
6	155-210	111	"

Experiment 10.—Antimonious Chloride.

25 c.c. of $n/10$ solution of antimonious chloride were taken, a large quantity of concentrated hydrochloric acid added, and then zinc chloride.

Fraction.	B. P. Liquid.	Temp. Vapor.	Sb in Distillate.
1	100°-110°	104°	Nothing.
2	110 -112	104 -107°	Trace.
3	112 -115	107 -108	"
4	115 -120	108	Distinct ppt.
5	120 -130	108	Larger "
6	130 -145	109	Much "
7	145 -210	110	" more "

During the seventh fraction a stream of hydrochloric acid gas was led through. Now additional concentrated acid was added and the distillation repeated with a stream of hydrochloric acid.

Fraction.	B. P. Liquid.	Temp. Vapor.	Sb in Distillate.
8	115°-125°	107°	Considerable ppt.
9	125 -145	108.5	" "
10	145 -170	112	" "

The combination of all the fractions in the above experiment showed that about two thirds or three fourths of the antimony had been distilled over, and by continued distillations with zinc chloride probably all would finally have been carried over.

Experiment 11.—Antimonious Chloride.

50 c.c. of the *n*/10 stock solution of antimonious chloride with the usual large amount of hydrochloric acid were taken, and in the latter part of the distillation a gram of sodium chloride was added.

Fraction.	B. P. Liquid.	Temp. Vapor.	Sb in Distillate.
1	110°	108°	Trace.
2	110	108	"
3	110	108	"
4	110	108	Little more than trace.

More hydrochloric acid here added and distillation continued in a stream of hydrochloric acid gas.

Fraction.	B. P. Liquid.	Temp. Vapor.	Sb in Distillate.
5	110°	108°	Trace.
6	110	108	"
7	110	108	"

More hydrochloric acid added and one gram of sodium chloride.

Fraction.	B. P. Liquid.	Temp. Vapor.	Sb in Distillate.
8	110°	108°	Trace.
9	110	108	"

Zinc chloride added with more acid and distillation continued.

Fraction.	B. P. Liquid.	Temp. Vapor.	Sb in Distillate.
10	110°-112°	108°	Trace.
11	112-115	108	More than trace.
12	115-125	108.5	Distinct ppt.
13	125-150	111	Large ppt.

Experiment 12.—Antimonious Chloride.

25 c.c. *n*/10 antimonious chloride solution taken in a large amount of hydrochloric acid as usual, then one gram of sodium chloride added.

Fraction.	B. P. Liquid.	Temp. Vapor.	Sb in Distillate.
1	110°	107°	Nothing.
2	110	107	"
3	110	107	"

Here zinc chloride was added and more acid.

Fraction.	B. P. Liquid.	Temp. Vapor.	Sb in Distillate.
4	110°	107°	Nothing.
5	111	108	Trace.
6	111-115 (Stream HCl)	108	"
7	115-120 " "	108-108.5	Distinct ppt.
8	120-125 " "	108.5	Large ppt.

Experiment 13.—Antimonious Chloride.

Took 25 c.c. of a 1 per cent. solution of antimonious chloride, added 50 c.c. of concentrated sulphuric acid, and 20 c.c. of concentrated hydrochloric acid. The liquid began boiling at 70° and rose rapidly to 117°. The vapor at this point was 100°. Time 2 or 3 minutes. No antimony had distilled over up to this point. Results from this stage on are as follows :

Fraction.	B. P. Liquid.	Temp. Vapor.	Sb in Distillate.
1	122°	108°	Traces.
2	130	107.5	Slight pp.
3	150	105	Larger "
5	175	105-104-105	Same.
5	200	106	Trace.
6	220	104.5	Nothing.
7	260	123	"

In all .0150 gram of antimony (calculated as metallic Sb) had distilled over up to this point. Now 50 c.c. more of hydrochloric acid were added and the distillation repeated.

Fraction.	B. P. Liquid.	Temp. Vapor.	Sb in Distillate.
1	98°	90°	Nothing.
2	117	106	Trace.
3	125	108	Slight ppt.
4	145	107	Larger ppt.
5	175	107-104-106	Less ppt.
6	220	105	Merest Trace.

Experiment 14.—Arsenious Chloride.

One gram of arsenious oxide, dissolved and oxidized by HCl and potassium chlorate was taken. Some zinc chloride added, then 15 grams of ferrous sulphate, and the distillation conducted with a stream of HCl gas.

The arsenious chloride began going over below 100° and at no time did the temperature rise above 112° for the liquid, and 108° for the vapor. After 40 minutes all but a trace of the arsenic had distilled over.

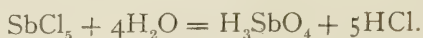
In reviewing these experiments the following conclusions may be deduced :—

Experiments 1 and 2 show that stannous chloride is entirely non-volatile up to a temperature of 150°, the traces of tin salt found in the distillate being in the stannic condition. This was doubtless due to oxidation of a small portion of the stannous chloride by the oxygen contained in the air in the flask, and in the water used to make the solution.

From Experiments 5, 6, 7, 8, 9, when antimony was distilled after oxidation by either nitric acid or potassium chlorate, it is seen that no antimony distils over till a temperature of 145° for the liquid and 108° for the vapor, the maximum for aqueous hydrochloric acid, is reached, and that even at considerably higher temperatures than this but little more than traces go over. It should be mentioned that when a temperature of 145° was reached in the liquid, only a very small amount of hydrochloric acid and water remained in the flask, the liquid being a very concentrated solution of the antimony, and the vapor having reached its maximum for aqueous hydrochloric acid from this point rose in temperature above this maximum.

The non-volatility of the antimony when oxidized to the pentad form is undoubtedly due to the formation of some one of the antimonious acids by hydrolysis of the antimonious chloride presumably

first formed by the oxidizing agent, as shown by the following reaction :



Antimony pentachloride formed by the treatment of metallic antimony by excess of dry chlorine gas is very volatile, distilling at a considerably lower temperature than the trichloride, and at the same time partially decomposing into the trichloride and free chlorine. If the pentachloride, however, is treated with excess of water, it forms a non-volatile solution, just as the solution of antimony made with hydrochloric acid and nitric acid, or potassium chlorate. This disposition to form an acid when oxidized to its highest state finds an analogy in phosphorus and arsenic, these forming in aqua regia phosphoric acid, and arsenic acid respectively. The same property is shown in bismuth, though in this case bismuth is so metallic in its properties that it is not oxidized to the pentad form in acid solution with aqua regia, or potassium chlorate. However, in alkaline solution, if free chlorine gas is added to the bismuth compound, bismuthic acid is formed, HBiO_3 . So here we have the analogy of all the elements of this periodic group when oxidized to the highest state in aqueous solution hydrolyzing to the acid, the tendency gradually decreasing from phosphorus down to bismuth, where it is almost lost.

The non-volatility cannot be due to the formation of a double chloride salt with potassium chloride as is stated by some chemists,¹ as in experiment 5 the temperature of volatilization was the same as in the other experiments where potassium chlorate was used as the oxidizing agent, and here no alkaline chloride was present to form a double chloride. The slight volatility of the antimony at the beginning of the distillation in experiments 8 and 9 was doubtless due to the incomplete oxidation of the large amount of antimony taken so that part was in the form of the trichloride, which at that temperature, as shown by the other experiments, is volatile.

From the results in experiment 3 it is seen that the stannic chloride volatilizes only when the temperature of the vapor rose above the boiling point of the dry salt. This vapor temperature was reached only when the temperature of the liquid reached some-

¹ Clowes and Coleman's Quantitative Analysis, p. 270, 3d ed.

where between 125° C. and 185° . The presence of hydrochloric acid seems to have no effect on the volatility of the stannic chloride. In experiment 4 it seems that the sulphuric acid converts the stannic chloride to a sulphate which is non-volatile at the temperatures of the experiment.

Experiments 10–13. The antimony in the trivalent form as chloride simulates arsenious chloride as to its volatility in aqueous hydrochloric acid, but is driven over much less rapidly and at a somewhat higher temperature, as seen by referring to experiment 14. Traces of antimony distilled over as soon as the temperature of the solution rose to the maximum for aqueous hydrochloric acid, but only in traces till the temperature of the liquid rose rapidly, and after the vapor had reached the point where its temperature began to rise above that of the maximum for aqueous hydrochloric acid.

In experiment 13, where sulphuric acid was added to raise the temperature, antimony distilled over slowly till practically all the hydrochloric acid had been driven over, and only antimony and sulphuric acid remained in the flask. The antimony then ceased to distil over, doubtless because of the formation of the sulphate of antimony which is non-volatile at the temperature attained. On the addition of a second portion of hydrochloric acid to the residue and redistilling, the antimony went over again as in the first distillation, it ceasing again to distil as soon as the hydrochloric acid had been boiled out. From this it would seem that the antimony in the experiment, when in the presence of strong hydrochloric acid, is in the form of a chloride, the condition as chloride or sulphate depending on which acid is in excess, thus obeying the law of mass action.

In experiment 12 it may be noticed that the presence of sodium chloride or other alkali chloride tends to retard the volatilization of the trichloride, so that at the maximum for aqueous hydrochloric acid no antimony distils over, or at least very inappreciable quantities. However, at a temperature for liquid of 112° and for vapor of 108° , the antimony chloride volatilizes as though no alkali chloride were present. This may be due to the formation of a double chloride of antimony and alkali which is slightly less volatile.

Perhaps, however, the explanation given by Richards¹ could be

¹ Quantitative Separation of HCN and HCl, *Am. Chem. Jour.*, 27, 208, 1902.

applied in this case, the addition of sodium chloride tending to increase the ionization of the antimony by driving back the ionization of the hydrochloric acid, and so rendering the antimony somewhat less volatile. Possibly the same theory would explain why arsenious chloride and antimonious chloride are volatile at in aqueous hydrochloric acid a lower temperature than their boiling points when dry.

CONCLUSIONS TO BE DRAWN FROM THIS WORK.

1. Antimony and tin may be separated from each other by distilling in an excess of aqueous hydrochloric acid, if the antimony is present as antimonious chloride and in very small quantities, and providing sulphuric acid is added to raise the boiling point, the antimony distilling over.

2. Antimony and tin may be separated from each other, if both are kept in the reduced condition, this being impracticable, however, as some tin is sure to become oxidized to stannic tin in the usual course of analysis, and volatilize with the antimony. If antimonious chloride and stannic chloride are together they volatilize at practically the same temperature.

3. Antimony oxidized by nitric acid, or by potassium chlorate in aqueous hydrochloric acid solution is totally non-volatile at the boiling point of the latter acid, due probably to the formation of antimonious acid, not antimonious chloride as is generally given, the former being non-volatile at this temperature.

4. The presence of a few grams of an alkali chloride as potassium chloride or sodium chloride slightly decreases the volatility of antimonious chloride solution, so that it may be boiled in excess of aqueous hydrochloric acid without fear of loss of antimony, if one of these alkali chlorides is added, or if potassium chlorate has been used in the oxidation.

5. The volatilizing point of arsenious chloride in concentrated hydrochloric acid, when it distils over in Fischer's distillation of arsenic, is at or below 108° C. for the vapor.

PART II.

AN INVESTIGATION OF HERROUN¹—WELLER'S² VOLUMETRIC METHOD FOR THE DETERMINATION OF ANTIMONY.

I. OXIDATION OF ANTIMONIOUS COMPOUNDS.

Historical.

THE various methods proposed for the volumetric determination of antimony all depend either upon the direct oxidation, or reduction of the antimony by the titrating solution; or indirectly upon the titration by sodium thiosulphate of iodine, liberated in the reduction (KI and HCl³), or oxidation (the iodic acid method⁴); or the titration of a product reduced by the antimony (as FeSO₄ by KMnO₄, etc.).

Evidently no method depending upon the reduction of antimony would be quantitatively accurate, unless the antimony first be brought completely into the highest state of oxidation. Potassium permanganate, potassium chlorate, nitric acid, and iodic acid, among others have been used as oxidizing agents either directly or indirectly.

Weller⁵ oxidizes antimony by potassium chlorate in hydrochloric acid solution. He does not state whether the oxidation is complete or not, but that he considered it complete is implied, as in the estimation of the antimony he adds potassium iodide, distils over the liberated iodine, which is then titrated by standard sodium thiosulphate, and the results are accurate.

Gautier⁶ oxidizes by potassium permanganate, and then titrates the iodine liberated, after addition of potassium iodide to the acid solution.

Causse³ oxidizes the antimony by means of iodine pentoxide (I₂O₅), and then titrates after distillation of the liberated iodine.

¹ Chem. News, 45, 101, 1882.

² Ann., pp. 362-369, 1882.

³ Ibidem.

⁴ Causse, Compt. Rend., 125, 1100, 1897.

⁵ Ann., pp. 362-366, 1882.

⁶ Actes Soc. Sci. Chili, 1897, 7, 74-76.

⁷ Comp. Rend., 1897, 125, 1100.

Quincke¹ uses potassium ferricyanide as oxidizing agent. Hanus² oxidizes the sulphide by means of ferric sulphate and titrates the reduced iron salt by means of potassium permanganate.

O. Bosek,³ in experimenting on the action of potassium chlorate and nitric acid in oxidizing antimony compounds, found that antimony could not be completely oxidized by either of these reagents. The best oxidation he could get by means of KClO_3 was 87.65 per cent. of the antimony oxidized. By the use of fuming nitric acid he could get only 98.23 per cent. oxidized. By the use of bromine in alkaline solution his results were as follows :

								Unoxidized.
4 hours boiling of the solution with bromine,								3.89%
10	"	"	"	"	"	"	"	1.51%
12	"	"	"	"	"	"	"	0.00%

This work of Bosek was so at variance with the work of others on the oxidation of antimony, that it was deemed desirable to investigate somewhat in detail the oxidizing effect of KClO_3 and HNO_3 on antimony.

Experimental.

As a basis of determining the degree of oxidation, potassium iodide in acid solution seemed to offer as convenient a reducing agent as any, and iodine in alkaline solution a satisfactory oxidizing agent. These were used as in the well-known method of Weller for the oxidized acid solution, and Mohr for the alkaline reduced solution.

Determination of Standard Sodium Thiosulphate and Iodine.

First attention was directed toward the preparation of reliable standard solutions of sodium thiosulphate, and of iodine. The sodium thiosulphate solution was checked against potassium bichromate, electrolytic copper, and resublimed iodine. The iodine standard was then carefully checked against this sodium thiosulphate.

(a) *Standardization Against Bichromate of Potash.*—Approximately .2000 gram of the bichromate, in which no impurities were found, dried at 130°C . till constant in weight, were weighed out, and dissolved in about 700 c.c. of water. First hydrochloric acid

¹ Zeits. f. anal. Chem., 30, 1-43.

² Zeits. f. anor. Chem., 1898, 17, 111-116.

³ Jour. Lond. Chem. Soc., 1895 (trans.), 515.

was used as the acidifying agent, starch as indicator, and 5 or more grams of potassium iodide added, and the freed iodine titrated by sodium thiosulphate till the solution was just changed from blue to the green of reduced bichromate. Results under these conditions were not concordant and were generally lower, when calculated to the antimony equivalent, than the standard by either copper or iodine. Finally the following conditions were found to give good results.

(1) Approximately .2000 g $K_2Cr_2O_7$, powdered and dried at 130° for 12 hours.

(2) 600 c.c. to 700 c.c. water.

(3) 3 grams of KI crystals added after acidifying.

(4) 15 c.c. of concentrated H_2SO_4 .

(5) 1 c.c. starch solution, added near the end of the titration.

With the sulphuric acid as acidifying agent the iodine was set free readily and a sharp end point obtained.

(b) *Standardization Against Copper*.—1000 to .1500 gram of pure copper foil was weighed out, dissolved in a small portion of nitric acid, evaporated very nearly to dryness on the water-bath (less than 1 c.c. of free acid), diluted to 10 or 20 c.c., made very slightly alkaline by dilute potassium hydrate, acidified by acetic acid, boiled for 2 or 3 minutes, cooled, diluted to 50 c.c. or 60 c.c., 2 or 3 grams of potassium iodide added, and titrated by sodium thio-sulphate.

(c) *Standardization Against Iodine*.—A portion of iodine (Kahlbaum) was resublimed with potassium iodide, dried over calcium chloride, and portions of this weighed out between small watch glasses, the glasses with the iodine placed in potassium iodide solution, the iodine dissolved, and titrated. Portions from the bottle direct gave the same results. So the original sample was considered pure.

RESULTS BY THE THREE METHODS.

Bichromate Method.

.1360 g. $K_2Cr_2O_7$	=	.0052910	$K_2Cr_2O_7$	per c.c. hypo.
.1400 g. "	=	.0052923	" "	" "
.1479 g. "	=	.0052910	" "	" "

Iodine Method.

.2630 g. Iodine	=	.013697	Iodine	per c.c. hypo.
.3831 g. "	=	.013692	" "	" "

Copper Method.

.2211	Copper	=	.0068664	Cu	per	c.c.	hypo.
.2054	"	=	.0068694	"	"	"	"
.2742	"	=	.0068550	"	"	"	"
.2749	"	=	.0068569	"	"	"	"
.2720	"	=	.0068600	"	"	"	"

The average for each method when calculated to the antimony equivalent is as follows, the atomic weights being taken as, Cu, 63.6; K, 39.11; Cr, 52.1; O, 16; I, 126.85 and Sb, 120.4.

Bichromate titration	=	.0064927	Sb	per	c.c.	hypo.
Iodine	"	.0064990	"	"	"	"
Copper	"	.0064947	"	"	"	"

TESTING THE OXIDATION AND THE CONDITIONS FOR TITRATION.

In selecting a solution of antimony on which to test the oxidizing power of potassium chlorate, and nitric acid, metallic antimony (Kahlbaum) was taken as the starting point. In making the solution no tartaric acid was used, thus avoiding a possible interference of this acid on the action of the oxidizing agents. A weighed portion of the powdered metallic antimony was weighed out in each experiment, and dissolved in hydrochloric acid, and one or both of the oxidizing agents, nitric acid or potassium chlorate. The free chlorine was driven out, the iodine liberated on the addition of potassium iodide to the acid solution was then titrated directly, using the standard sodium thiosulphate that had been checked against copper, potassium bichromate, and iodine as indicated above. If the portion of antimony taken had been oxidized completely to antimonic acid, then on adding an excess of potassium iodide, an amount of iodine should be set free, which on being titrated with sodium thiosulphate should indicate the same quantity of antimony as was taken in the first place, providing of course, the hydriodic acid from the acid potassium iodide solution had reduced the antimony completely, the antimony contained no impurities to interfere, the hydrochloric acid had no decomposing effect on the hydriodic acid liberated, and there had been no loss by volatilization or otherwise in getting the solution and oxidation of the antimony.

As a preliminary experiment three samples of antimony were taken, dissolved in about 1 c.c. of nitric acid, and 50 c.c. of concentrated hydrochloric acid, and boiled for some time, then another 1

c.c. of nitric acid, and more hydrochloric acid were added and boiled till complete removal of the free chlorine, more hydrochloric acid being added as was necessary to complete the decolorization of the solution. Finally the solution was evaporated to about 50 c.c., diluted to 600 c.c., 3 grams of potassium iodide added and the liberated iodine titrated.

The results were as follows :

Sb taken.	Sb found.	Per cent. of Error.
.2232 g.	.2098	6.00 % low.
.2037 "	.1971	3.20 " "
.2572 "	very low.	

In the course of the above titrations, though no oxychloride was formed on diluting the solution with water, as above indicated, yet when potassium iodide was added and the sodium thiosulphate run in, a white and sometimes a yellow precipitate formed. So it was seen to be necessary to have a larger amount of hydrochloric acid present before beginning the titration. On examination of the precipitate referred to, it was found to be SbOCl , if white, and a mixture of SbOCl and SbOI , if yellow.

Effect on the Titration of Varying the Strength of the Hydrochloric Acid.

A few experiments were made to determine how strongly acid the solution could be made, and yet not liberate iodine by the acid in the course of the titration, and so vitiate the results.

The hydrochloric acid taken contained no free chlorine, as a portion from the bottle was boiled for some time, and the boiled sample gave results similar to that which had not been boiled.

Results were as follows :

1. 400 c.c. H_2O , 3 grams KI, 10 c.c. HCl. No blue color to starch after standing 10 minutes.
2. 400 c.c. H_2O , 3 grams KI, 20 c.c. HCl. No blue after standing 10 minutes.
3. 400 c.c. H_2O , 3 grams KI, 30 c.c. HCl, $\frac{1}{10}$ c.c. hypo. $n/10$ to decolorize, in 10 minutes.
4. 400 c.c. H_2O , 3 grams KI, 40 c.c. HCl. Iodine given off from the first.
5. 400 c.c. H_2O , 3 grams KI, 20 c.c. HCl. Only faint blue after standing 20 minutes.

6. 400 c.c. H_2O , 3 grams KI, 30 c.c. HCl. In 30 minutes gave iodine equivalent to .30 c.c. hypo.

These results show that it is unsafe to have more than 20 c.c. of concentrated hydrochloric acid present to 400 c.c. of water in the ordinary direct titration of antimony.

Effect of the Liberation of Iodine on Heating the Hydrochloric Acid and Potassium Iodide Solution.

1. 500 c.c. H_2O , 3 grams KI, 30 c.c. HCl. Iodine set free rapidly as soon as warmed.

2. 500 c.c. H_2O , 3 grams KI, 20 c.c. HCl. About same as No. 1 above.

3. 500 c.c. H_2O , 3 grams KI, 10 c.c. HCl. Considerable iodine set free before the solution came to a boiling temperature.

4. 500 c.c. H_2O , 3 grams KI, 5 c.c. HCl. Iodine free before liquid boiled.

From this it is seen, that on boiling a hydrochloric acid solution containing potassium iodide, iodine is set free even from very dilute solutions. So in Weller's method of distilling over the iodine before titration in antimony determinations, it would seem doubtful if the iodine given off was equivalent to the antimony reduced alone, for the hydrochloric acid would liberate some iodine also.

For this reason all the titrations of the antimony were made directly, without distillation, in the cold antimony solution.

Effect on the Titration of Varying the Amount of Potassium Iodide.

Three portions of antimony, (a) .2151 g., (b) .2473 g., (c) .2201 g. were taken, dissolved in aqua regia, excess of chlorine boiled out as usual, evaporated to 50 c.c., then 15 c.c. of hydrochloric acid added, and diluted to 700 c.c. To (a) .7 gram of potassium iodide was added and titrated. Iodine was liberated slowly, and no distinct end point was reached, as the reduction seemed to be slow, and the color kept coming back after the end seemed to be reached. To (b) 1.5 grams of potassium iodide was added. A better end point here was obtained, but the blue color would soon return. Reduction yet was slow. To (c) 3 grams of potassium iodide were added. The iodine was liberated quickly and a sharp end point was found. No return of color was noticed for a considerable time after the end of the titration.

The conditions thus shown for the titration of antimony by this method are within rather narrow limits and are as follows :

To .2000 gram of antimony (metallic) dissolved and oxidized by nitric acid and hydrochloric acid, or potassium chlorate and hydrochloric acid. The solution is then concentrated to about 50 c.c. This solution would be about 20 per cent. hydrochloric acid. To this must be added about 15 c.c. to 20 c.c. of concentrated hydrochloric acid, and the whole diluted to 600 c.c. or 700 c.c. Three grams of crystals of potassium iodide are then added, the liberated iodine titrated nearly to the end, 1 c.c. of starch solution introduced and the titration completed, *i. e.*, to no blue color. End point is very sharp.

Having determined what seemed to be favorable conditions for this titration, a large number of determinations of antimony were made. A weighed portion of metallic antimony was taken, 1 to 2 c.c. of concentrated nitric acid and 50 c.c. or more of concentrated hydrochloric acid added, then boiled until the chlorine was partially removed, portions of $\frac{1}{2}$ gram or less of potassium chlorate then added and free chlorine boiled out. Finally more hydrochloric acid was added and the solution concentrated to 50 c.c. or 60 c.c. The other conditions as to dilution, amount of potassium iodide added were as above given. The use of nitric acid and potassium chlorate would seem to be the strongest oxidizing mixture we have, so in most subsequent experiments the two were used, though the results of titration were the same if only nitric acid were used. It is desirable to use a small amount of nitric acid in every case, however, as metallic antimony dissolves very slowly in potassium chlorate and concentrated hydrochloric acid alone.

The results of a large number of titrations were found to be as follows :

Sb taken.	Sb found.	Per cent. of Error.
.1781 g.	.1766	.85 % low.
.1883 "	.1868	.84 " "
.2119 "	.2098	.99 " "
.2224 "	.2202	.99 " "
.2306 "	.2289	.73 " "
.2055 "	.2033	1.05 " "
.1358 "	.1341	1.25 " "
.1505 "	.1487	1.19 " "
.1547 "	.1535	.77 " "
.1451 "	.1432	1.50 " "

Sb taken.	Sb found.	Per cent. of Error.
.1400 g	.1387	.92 % low
.1587 "	.1565	1.32 " "
.1557 "	.1539	1.16 " "
.1962 "	.1938	1.22 " "
.2508 "	.2480	.88 " "
.2626 "	.2602	.90 " "
.2179 "	.2161	.85 " "
.2284 "	.2261	.99 " "
.1941 "	.1918	1.18 " "
.2476 "	.2452	.96 " "
.2095 "	.2068	1.29 " "
.1975 "	.1951	1.21 " "
.1900 "	.1893	.37 " "
.2065 "	.2048	.82 " "
.1893 "	.1873	1.08 " "
.2220 "	.2198	.96 " "

These experiments showed an error of 1 per cent. on an average, which at first was thought to indicate incomplete oxidation. To show, however, that this was not the case, a number of experiments were performed, when weighed portions of antimony were dissolved and oxidized as in the above determinations, tartaric acid added, neutralized nearly by sodium carbonate, and rendered alkaline by an excess of sodium bicarbonate as is usual in Mohr's titration method. The alkaline solution was then titrated by standard iodine. Blanks were also run where about the same amount of hydrochloric acid was taken as in making the antimony solution, this boiled with 1 c.c. concentrated nitric acid and small portions of potassium chlorate, chlorine boiled out, tartaric acid added, rendered alkaline, and titrated by iodine, results as follows :

Sb Taken.	c.c. Iodine used.	Sb indicated.	Per cent. Sb Equivalent.
.2765	0.30	.001326	0.45
.2515	0.20	.000884	0.35
.2093	0.15	.000633	0.30
.1663	0.20	.000884	0.50

The average of several blanks gave :—

0.15 iodine = .000633 Sb.

On the supposition that an antimonious salt in alkaline solution is completely oxidized on titration by iodine, the results of the above work would undoubtedly show that antimony is completely oxidized to the highest state by potassium chlorate and nitric acid

in hydrochloric acid, or at least within the limits of experimental error. I was unable to understand the results of Bosek given on page 18.

2. TESTING FOR IMPURITIES IN THE SAMPLE OF ANTIMONY USED.

The almost constant error of 1 per cent. low in the titrations of antimony therefore was not due to incomplete oxidation. A series of investigations were now made in the hope of discovering the cause of the error. Naturally it was thought to be due to an impurity in the antimony sample, so a number of tests were very carefully carried out to find the impurity if possible. The sample of antimony was "Kahlbaum's best," and it was hardly expected to be impure. The following materials were most carefully tested for: sodium, potassium, copper, bismuth, lead, silver, tin, iron, phosphorus, sulphur and oxygen. Among these only a trace of iron was found. This however would give high results in the titration, and not low, as was constantly found. Arsenic would also give high results if present. The oxygen was tested for by making a combustion of the sample in a stream of hydrogen. No impurities being found, attempts to make metallic antimony from recrystallized tartar emetic were made, so as to compare results of the titration on this sample.

First "c. p." tartar emetic recrystallized three times was heated in air, till a mass of metallic antimony and antimony oxide had formed, then this mass was fused with potassium cyanide. This sample was found to contain about 2 per cent. of impurity, potassium as one part. Next antimony was obtained by the direct fusion of the tartar emetic. Two samples made by this method, on titration by the same method as above, gave .92 per cent. low and .74 per cent. low respectively. Potassium was tested for in these samples and none found. Still another sample of antimony was made by producing antimony hydride by zinc and acid in the ordinary Marsh apparatus, this decomposed in a tube at red heat, and the metallic antimony deposited, then titrated. The usual 1 per cent. low resulted in this sample as in the others.

From the tests it seemed impossible that the error was due to an impurity.

3. TESTING FOR VOLATILIZATION OR MECHANICAL LOSS.

The vessel used in making the solution of the antimony in most of the above experiments was a beaker of about 800 c.c. capacity, covered with a watch glass. Thinking that there might be mechanical loss in boiling, several samples were dissolved and oxidized, using instead of the beaker a long-necked Kahldahl flask. The solution was then titrated. The usual 1 per cent. low was found.

To more carefully test the volatility of the antimony in going into solution, samples were dissolved in the above flask, connected with a condenser and all products distilling over collected in a vessel of water, the delivery tube dipping into the liquid. To this water and distillate was added a few cubic centimeters of sulphuric acid, evaporation made on a water-bath, till most of the water, hydrochloric and nitric acid had evaporated. The residue gave no test for antimony. Two samples of antimony from which the distillate had been thus collected and tested gave when titrated 1.06 per cent. low, and 1.20 per cent. low respectively. The low results evidently were not due to volatilization, which again confirms the results obtained in testing the non-volatility of antimonious acid recorded in the first part of this paper.

Determination of Antimony Electrolytically.

To still further test whether the sample weighed out in each titration contained actually as many milligrams of antimony, as the weight indicated, a number of samples were weighed, dissolved and oxidized as usual, titrated without starch as indicated, the antimony then precipitated by sulphuretted hydrogen, this sulphide dissolved by sodium sulphide and electrolyzed.

Conditions of the electrolysis were as follows :

- (1) 50 c.c. of a saturated solution of sodium sulphide.
- (2) 30 c.c. of water.
- (3) 60 c.c. to 70 c.c. of a 20 per cent. solution of sodium sulphite.
- (4) This mixture with the antimony warmed till colorless in a platinum dish.
- (5) One series was electrolyzed at 60° C. for 3 or 4 hours with a current of 0.7 to 1.00 ampère. The other series electrolyzed at the ordinary temperature with current of 0.25 ampère over night.

Results of series electrolyzed at 60° C.:

Sb Taken.	Sb Found by Titr.	Per Cent. Error by Titr.	Sb Found by Elect.	Error by Elect.
.2140	.2119	.90 low.	.2166	1.2 high.
.2316	.2292	1.00 "	.2318	0.0 "
.2825	.2795	1.03 "	.2844	.67 "

Electrolyzed at ordinary temperature :

Sb Taken.	Sb Found.	Per Cent. Error.
.2258	.2262	0.00
.2743	.2747	0.00
.2136	.2150	.65 high.
.2227	.2243	.75 "

It was very difficult to get good results by electrolyzing under these conditions, and these seem to be the most favorable yet known. The results were not concordant, though if they show anything, it is that the antimony was present as weighed out. The deposit in all these cases was well adherent and of dull metallic luster. There is a great tendency to deposit sulphur, however, and the method seemed to be rather unreliable as a check.

4. REDUCTION OF ANTIMONY TO THE TRIVALENT FORM.

Historical.

The work so far gives no explanation of the one per cent. error. It could yet be due to at least one other cause, viz., incomplete reduction by the hydriodic acid. Indeed complete reduction of antimony has been found to be difficult especially when boiled with sulphur dioxide, or sodium sulphite in acid solution, as is most usual in getting the antimony in condition for Mohr's titration.

Knorre¹ states that good reduction of antimony by sodium sulphite in acid solution is not possible in an open vessel, but by adding a small amount of sodium sulphite to the acid solution in a bottle, then closing the bottle and heating on a water-bath, thus allowing the sulphur dioxide to act under considerable pressure, the reduction is complete.

Clark² found that antimony ores, if dissolved by hydrochloric acid in the presence of iodine, are oxidized only to the trivalent form, and if after boiling out the excess of iodine, or titrating the lost traces of iodine by sodium sulphite, the solution is neutralized and titrated by iodine, good results could be obtained.

¹ Zeits. Angn. Chem., 155-157, 1888.

² J. S. C. I., 1896, 255-257.

Gooch and Gruener¹ reduced the solution by boiling it with potassium iodide in acid solution, taking up the last traces of iodine with sulphur dioxide. They considered the reduction complete.

M. Rohmer² says antimony cannot be completely reduced by boiling with sulphur dioxide alone, but if one gram of potassium bromide is added with the sulphur dioxide, the reduction is complete.

Experimental.

Testing Methods of Reduction.

(a) *Sulphur Dioxide in Open Vessel.*—In these experiments the metallic antimony was dissolved in hydrochloric acid, nitric acid and potassium chlorate as usual in a tall beaker covered with a watch glass. After boiling out the free chlorine, 30 c.c. of an approximately 5-per-cent. sulphur dioxide solution were added, most of the free sulphur dioxide removed by boiling, then 30 c.c. more of the sulphur dioxide added, and boiled out completely. Two grams of tartaric acid were then added, solution made alkaline by sodium bicarbonate and titrated by standard iodine. The iodine standard had been carefully checked against the sodium thiosulphate solution used in all the previous titrations.

Results as follows :

Sb Taken.	Sb Found.	Per Cent. Error.
.2075	.2055	.96 low.
.1817	.1794	1.26 “
.1963	.1940	1.12 “

(b) *Sulphur Dioxide in Closed Vessel.*—Two experiments were made when the oxidized solution was placed in a strong bottle, 60 c.c. of the sulphur dioxide solution added, the bottle closed gas-tight and heated for an hour immersed half way in a water-bath. The sulphur dioxide then boiled out, tartaric acid added, made alkaline and titrated by iodine. Results :

Sb Taken.	Sb Found.	Per Cent. Error.
.1706	.1684	1.20 low.
.2262	.2232	1.30 “

(c) *Precipitation as Sulphide and Solution in HCl.*—In this experiment the antimony was dissolved as usual and titrated by sodium

¹ Am. Jour. Sci., 3, 42, 213-220.

² Ber., 1901, 34, 1565.

thiosulphate, the antimony precipitated by hydrogen sulphide, this dissolved in concentrated hydrochloric acid, the hydrogen sulphide removed by warming (not boiling), tartaric acid added, etc., and titrated.

The reduction here depends on the fact generally recognized that antimony precipitated in the form of antimony pentasulphide is converted to antimony trichloride by solution in hydrochloric acid, sulphur being freed in equivalent amount.

Sb Taken.	Sb Found by Hypo.	Per Cent. Error.	Sb by Iodine.	Per Cent. Error.
.2065	.2242	1.10 low.	.2048	.87 low.

(d) *Reduction by Sulphur Dioxide and Potassium Bromide.*—The solution was treated with 40 c.c. of the sulphur dioxide solution and 1 gram of potassium bromide, as suggested by Röhmer (reference given above). The sulphur dioxide was then boiled out and the antimony titrated by iodine.

Sb Taken.	Sb Found.	Per Cent. Error.
.2495	.2465	1.2 low.

By these other methods of reduction it is seen that no higher results were obtained than had been secured by the sodium thiosulphate titration, and consequently if the low results were due to incomplete reduction, no better results could be obtained by these means than by potassium iodide in cold acid solution.

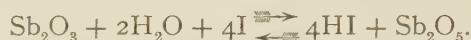
(e) *Reduction by Potassium Iodide in Acid Solution by Boiling.*—A few experiments were made where two or three grams of potassium iodide were added to the oxidized solution and the liberated iodine distilled over, thus hoping to get better reduction by the boiling hydriodic acid solution. The difficulty of driving the last portions of iodine over here were considerable, so that in each case the last portions of iodine in the solution had to be taken up with sulphur dioxide, or sodium thiosulphate before neutralization. This introduced a complication that made the method uncertain and concordant results difficult to obtain.

(f) *Effect of Largely Increasing the Potassium Iodide.*—It was thought that possibly better reduction (if indeed it was not already complete) would be obtained by adding larger amounts of potassium iodide before titrating with sodium thiosulphate. In these experiments the condition as to the amount of hydrochloric acid was the

same as in all other sodium thiosulphate titrations. The results were as follows :

Sb Taken.	KI Added.	Sb Found.	Per Cent. Error.
.2205	1 gram.	.2176	1.32 low.
.2470	2 "	.2440	.91 "
.2230	2.5 "	.2208	.96 "
.2280	5 "	.2259	.91 "
.2459	5 "	.2436	.92 "
.2276	10 "	.2265	.48 "
.2111	10 "	.2094	.80 "
.2610	10 "	.2594	.59 "
.2152	20 "	.2142	.47 "
.2665	20 "	.2651	.51 "
.2214	20 "	.2208	.30 "
.2578	40 "	.2578	.00 "
.2273	40 "	.2275	.00 "
.2417	60 "	.2424	.38 high.

It was at first thought that possibly the iodine freed by adding the potassium iodide to the antimonious compound formed a balanced reaction with the antimony as in the equation



If such a balance should be established the amount of iodine thus made to reoxidize antimony would depend upon the concentration of the hyriodic acid in the solution. By increasing this concentration by the addition of a larger quantity of potassium iodide, it was hoped that finally a point would be reached where an amount of iodine would be freed exactly equivalent to the antimony. The results, as seen from the table, seemed to bear out this view till the last experiment was performed, when it was seen that too large an amount of iodine had been freed. Then a number of blanks were run where in each case 700 c.c. of water were acidified with hydrochloric acid to the same degree as in the usual sodium thiosulphate titrations, and the amount of potassium iodide varied. The iodine liberated was taken up by sodium thiosulphate. The results were as follows :

H ₂ O	HCl	KI	Iodine After 10 Minutes' Standing.
700 c.c.	30 c.c.	3 grams.	0.00
700 "	30 "	10 "	.10 c.c. hypo.
700 "	30 "	20 "	.20 " "
700 "	30 "	40 "	.40 " "
700 "	30 "	60 "	.70 " "

On the basis of .2000 gram antimony taken .4 c.c. of the sodium thiosulphate would be equivalent to about 1.2 per cent. of antimony. These results showed that as the concentration of the hydriodic acid was increased iodine was liberated in increasing amounts, probably due to the action of the hydrochloric acid on the hydriodic acid, this being what caused the higher results in the titrations of the antimony.

The foregoing experiments lead to the conclusion that the reduction of antimony by hydriodic acid as in the sodium thiosulphate titration is as complete as by the other methods, and that the reduction is complete in all. However Weller in his original paper states that he obtained good results when he distilled over the iodine and titrated it. Also Herroun¹ by direct titration considers the method accurate. These higher results may be accounted for easily, when it is noticed, as in Weller's method, that on heating a solution of potassium iodide acidified with hydrochloric acid (see page 17) a considerable amount of iodine is set free even when no antimony is present to be reduced, and when the very strongly acid solution of the antimony used by Herroun is taken into account. In a few experiments tried to determine whether higher results would be obtained with stronger acidification, it was found that as the amount of acid was increased higher results were obtained till, when 150 c.c. of concentrated hydrochloric acid was added to 600 c.c. of the solution of antimony, the titration gave exactly theoretical results.

THE ATOMIC WEIGHT OF ANTIMONY.

In the light of the work thus far done, I was unable to account for the one per cent. error. The experiments seemed to show that (1) the antimony is completely oxidized by nitric acid and potassium chlorate; (2) that by adding 3 grams, or more, of potassium iodide to the properly acidified solution of the antimony, there is complete reduction; (3) that in making the solution there was no loss of antimony mechanically, nor by volatilization; (4) that there was no recognizable impurity in the antimony sample that would tend to lower the results of the titration.

There seemed to be but one way left to account for the one per cent. error, *i. e.*, the atomic weight of antimony. I do not advance

¹ Chem. News, 1882, 45, 101.

the work recorded in this paper as definite proof that the atomic weight of 120.4, as used in all the calculations herein recorded, is too low. It should be noted, however, that Gooch and Greuner¹ found the standard of sodium thiosulphate when checked against tartar emetic, differed by about .5 per cent. on the basis of .2000 gram of antimony, and that antimony determined by the sodium thiosulphate standard checked against arsenic was .5 per cent. low. Then when we consider that the determination of the atomic weight of antimony from time to time has given divergent values, and that at present the best authorities differ by about .80 (119.92, Cook; 120.7, Popper), we might be justified in suggesting that the atomic weight of 120.4 is possibly too low. To account for the entire error of one per cent. an atomic weight of 121.5 would need to be given to antimony when calculated on the oxygen basis.

I am unable to explain why the standards made against copper, potassium dichromate, and iodine should all agree well, but when made against the best antimony I could get, there should be such a discrepancy as herein shown, especially when the end point in each case was the same, *i. e.*, sodium thiosulphate, iodine, starch.

Attention should be called to the following data in reference to the atomic weight of antimony as determined by various chemists.

Berzelius obtained 129. By the reduction of the sulphide Schneider² found 120.53. Dexter,³ Kessler,⁴ and Dumas⁵ each arrived at a number slightly above 122, the first by the oxidation of antimony by nitric acid, and weighing as Sb_2O_4 , the second by oxidation by potassium chlorate and potassium chromate in acid solution, and the third by titration of the chloride by silver nitrate.

Cook⁶ in the analysis of the bromide found 119.99. A little later Pfeifer⁷ by the simultaneous electrolysis of a solution of silver, and of antimony chloride found for antimony an average of 121, and Popper⁸ by the same method found 120.7 as an average.

¹ Am. Jour. Sci., 3, 42, 213-220.

² Pogg. Ann., 98, 293, 1856; J. pr. Ch. (2), 22, 131, 1880.

³ Ibidem, 100, 563, 1857.

⁴ Ann. Chim. Phys. (3), 55, 129, 1859.

⁵ Pogg. Ann., 113, 145, 1861.

⁶ Lill. Am. Jour. (3), 15, 41 and 107.

⁷ Ann., 209, 173, 1881.

⁸ Ibidem, 233, 152, 1886.

Bougartz¹ arrived at 121.2 to 120.5. These are all calculated on the oxygen standard of 16.

ACCURACY AND ADAPTABILITY OF THE HERROUN METHOD FOR ORDINARY USE.

Of the volumetric methods for antimony the direct titration of the iodine liberated by the addition of potassium iodide to antimony solution after oxidation by nitric acid and potassium chlorate in hydrochloric acid solution, no tartaric acid being used, gives as accurate results as Mohr's method, and the method is much simpler to carry out. Tin, if present, does not interfere, as it would be oxidized to the stannic condition, and is not reduced by hydriodic acid. This was shown to be true by a number of experiments where tin was added to the antimony.

The 1 per cent. error constantly found, it will be noticed, is calculated on metallic antimony and in the analysis of an ore if only 25 per cent. or less of antimony is present the method would be within the limits of error in technical work. For great accuracy a correction of 1 per cent. on the percentage found can be made.

Two ores analyzed gave as follows :

Ore Taken.	Per Cent. Sb Found.
(1) .9847	18.65 Per Cent.
(2) 1.0462	18.68 "
(3) .8966	18.63 "

The ore contained arsenic and iron. In the first two cases the arsenic was distilled over by Fischer's distillation, the antimony then precipitated by hydrogen sulphide ; this sulphide dissolved by HCl, HNO₃, KClO₃ and titrated as usual. In the third case the arsenic was separated by precipitation in 1.17 sp. gr. solution of hydrochloric acid. A gravimetric determination on this ore gave 18.74.

Another ore containing no arsenic gave results as follows : 45.35 per cent., 45.21 per cent., 45.25 per cent. There is no trouble whatever to get concordant results and the end point is all that may be wished.

DIRECT TITRATION OF ANTIMONY BY POTASSIUM PERMANGANATE.

Petriccioli² and Reuter determine antimony by oxidation of the reduced antimony by potassium permanganate in hydrochloric acid

¹ Ber., 16, 1942, 1883.

² Zeits. für Ang. Chem., 1901, 1179.

solution. A number of titrations were made to test the character of the end point, using an approximately $n/10$ potassium permanganate solution. The antimony in the form of antimonious chloride solution was diluted with water, after acidifying with hydrochloric acid till a slight cloudiness was seen, then just enough acid added to take up the cloudiness. The solution then titrated by the permanganate solution. No definite end point could be reached. Oxidation at the last seemed slow and the pink constantly disappeared. The titration was also tried in sulphuric acid solution of antimony. The results were no better. Finally a large portion of manganese sulphate was added to the solution before titration, if possible, to neutralize the effect of the hydrochloric acid on the permanganate. No better end point was found. An empirical end point might be established, but the method would be uncertain and is not to be recommended.

CONCLUSIONS.

The conclusions to be drawn from this work are :

1. Antimony is completely oxidized by nitric acid and potassium chlorate in hydrochloric acid solution, in the absence of tartaric acid.
2. Antimony is completely reduced by boiling with sulphur dioxide in open or closed vessel ; or by sulphur dioxide and potassium bromide ; or by potassium iodide in cold hydrochloric acid solution.
3. The direct titration of antimonious solutions by Herroun's method gives very concordant results, but is 1 per cent. low, calculated on metallic antimony with atomic weight 120.4.
4. The conditions for getting this result must be within rather narrow limits and are as follows :
 - (a) .2000 to .2500 gram antimony (calculated as metal).
 - (b) Oxidized and dissolved by hydrochloric acid, 1 c.c. nitric acid, and successive portions of potassium chlorate, in the absence of tartaric acid, solution reduced to 50 c.c., and 15 c.c. or 20 c.c. of concentrated hydrochloric acid added, then made up to about 700 c.c. by the addition of water.
 - (c) 3 or 4 grams crystals of potassium iodide added to the cold solution.
 - (d) Liberated iodine immediately titrated by sodium thiosulphate checked against copper, potassium bichromate, or iodine.

5. The error of 1 per cent. low not yet accounted for unless there is an error in the atomic weight of antimony.

6. The permanganate titration of antimony is of doubtful utility as an accurate and convenient method.

BIOGRAPHICAL.

Lewis Addison Youtz entered Simpson College, Iowa, in 1884, graduating in 1890 with the degree of Ph.B. The degree of Master of Philosophy was conferred upon him in 1893, and Master of Science in 1902, by the same institution.

1890-1900 was spent in teaching as follows :

1890-1891, Principal of the High School, Altoona, Iowa.

1891-1893, Instructor of Natural Sciences in the High School of Des Moines, Iowa.

1893-1899, Associate Professor of Natural Science (chemistry and botany), Simpson College, Iowa.

1899-1900, Professor of Science, Montana Wesleyan University.

During 1900-1902 he pursued post-graduate studies in chemistry under the Faculty of Pure Science of Columbia University, leading to the degree of Doctor of Philosophy.

Publications: "Clays of the Indianola (Iowa) Brick, Tile and Pottery Works," read before the Iowa Academy of Science, 1895.

"Analysis and Description of the Indianola (Iowa) Mineral Waters."

"Entomostraca (classification and habits) of the Mountain Lakes of Northwest Montana," Bulletin of the State University of Montana.

